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Ab Initio Study of Alkali Atoms Intercalation in Transition Metal Dichalcogenides

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With ab initio density functional theory adsorbate behaviour on layered crystals of $TiSe_2$-type is studied. Diffusion at the surface and into the substrate is quantitatively determined.

1 Introduction

The term "transition metal dichalcogenide (TMDC)" sounds too strange to associate anything of technical importance with it compared to common metals, graphite, silicon, high temperature superconductors etc.. So, we are not claiming that these compounds as e.g MoS_2 – lubricant additive to car engine oil and widely used to loosen rusty and corroded machine parts, for those readers who still remember the ugly stains obtained on their shirts even when trying to solely distribute it on those special objects – are of similar importance. The catalytic properties of the TMDCs are recognized in the business of petrochemistry, but not in household appliances of course. Also, electrochemical photocells of WS_2 offer an extremely high conversion efficiency of light to chemical energy, and the manufacturing of Li/TiS_2 intercalation batteries may deserve serious consideration. *Intercalation* is called the transport process which transfers an adsorbed molecule from the surface into the interior of the crystal where in the case of TMDCs wide gaps between the layers exist. So, we are far away from considering TMDCs as the ultimate necessity of industrial development. Nevertheless, they seem to be helpful materials.

Apart from the above ideas to convince a funding corporation of the practical importance, a sponsor might have some friendly inclination towards basic research. There, the TMDC community can refer to the quasi two-dimensionality of these substances which is almost unique though not so common as that of graphite. They show charge density waves with interesting structural phase transitions which led to puzzling questions in the 1970's and still raise new ones as proves a recently detected kind of self-organisation in separating two TMDCs as pure phases from their mixture. Similarly, partly self-organised nano-structuring at TMDC surfaces could be claimed when wire-like networks were observed, see Fig. 1. One could also mention that the TMDCs are easily cleaved – that is because of their two-dimensionality – which, when done under ultra high vacuum, gives rise to extremely clean ideal surfaces, thousands of Angstroms without any fault not to say "as far as the scanning tunneling microscope's (STM) eye can look". So, it is obvious that the TMDCs' surfaces are an ideal substrate for surface physics and chemistry, be it for investigating adsorbates and their interaction, be it for growing new materials.

Theoretical investigation of electronic behavior must give the clue for the phenomenology of the TMDCs. Total energy landscapes on parameter space which via optimization decide on the geometric structure and specific geometric developments in non-equilibrium

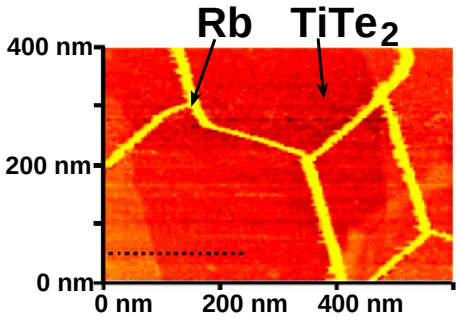

Figure 1. Network of alkali wires on TMDC, here Rb on $TiTe_2$(0001) surface[1].

situations should be understood in electronic terms reflected by the density of states resolved with respect to atomic orbitals, to constituting layers, or to momentum as condensed in various bandstructures. There exist many, many ab initio density functional theory (DFT) calculations, very valuable but mostly not concerning TMDCs besides some solitary ones. Thus, we tried to add to those few. After introducing in the next two sections the method and the material we present in the subsequent section a study of atom adsorption and diffusion on plain surfaces and in the intersandwich gap. It is followed by the investigation of intercalation from the plain surface and by a further section on intercalation via a different path, namely diffusion over surface step edges. The last section discusses the possibility of general chemisorption on TMDCs with the goal to grow new materials.

2 Motivation

From the importance of the transition metal dichalcogenide for surface physics and surface chemistry and the up to date still very uncomplete understanding with partly contradictory results it is highly suggestive to start with ab initio computations to clarify the picture from the point of view of theory. Adsorption of atoms and molecules on such surfaces, their intercalation, and their assembly to larger units such as clusters or whole monolayers represent the very first steps on the path to explain nanoscale growth with its many facettes as the self-organization to bulk phase separation or surface pattern formation of nano-wire networks. It also lies at hand to begin the investigations of adsorption with alkali and noble metal atoms, where experimental work to compare with is available, and to extend later to larger molecular groups.

3 Density Functional Theory Method

3.1 The Code

In view of the many presentations of density functional theory (DFT) and of those using DFT, e.g. also in this volume, we will not describe the details of the method. Our own experience of program development relies on the linearized augmented plane wave (LAPW)

method[2] which we did not use in the context of the present computation. LAPW codes use an all-electron basis and are highly accurate but also time consuming. The pseudopotential codes are fast, but the construction and reliability of the pseudopotential needs careful preparation and handling. We found the code of the Scheffler group[3] excellently suited for the purpose of this project. Once the atomic pseudopotentials have been generated the code can be comfortably managed and flexibly applied to various tasks.

For the pseudoptentials several choices had been investigated finally deciding in favor of the Troullier-Martins[4] development. It is standard to some extend but one has to clear the transferability of the potentials by applying it to various test cases. General physical properties as the absence of ghost states in the valence energy range have to be considered. Transferability refers to the property that the potential of an atom is well suited for a lot of chemical environments of molecules or solids. As the pseudopotential replaces the inner shell electrons by an effective potential, the transferability is checked through calculating atomic excited states and comparing with all-electron results. Besides this, calculation of simple solids containing this atom as e.g. the elemental solid and comparison with experiment is even a more realistic test of transferability.

The code utilizes supercells, i.e. the Hilbert space is spanned by periodic functions whose period corresponds to the largest computationally manageable unit cell which reasonably simulates the physical solid. In detail, the semi-infinite solid with surface is replaced by a slab infinitely repeated along the surface normal direction. In the surface parallel directions the physical unit cell of the ideal periodic solid is taken or a fictious unit cell truncating and repeating the special considered part of a solid with inhomogeneities. A sufficient thickness of the slab should guarantee that both surfaces decouple and the splitting of the states belonging to the doubling of the surface in comparison to the semi-infinite crystal can be well controlled, otherwise the second surface has to be kept inert by saturating the bonds with Hydrogen or similar. The calculation scheme affords a fully self-consistent relaxation of the electrons and full relaxation of the atomic position using damped molecular dynamics.

3.2 Computational Details

Equilibrium configurations were calculated by minimizing the total energy, propagation paths of particles also were determined by the energy of consecutive minima. For uphill diffusion, either a sufficient set of positions were assembled to obtain a three-dimensional energy landscape or we started with a first guess for the saddle point and let diffuse the particle downhill.

In our ab initio total energy calculations the forces necessary to integrate the classical equations of motion were determined by density functional theory calculations. The exchange-correlational functional was treated in the local density approximation. The Kohn-Sham equations are solved by a Car-Parinello-like iterative scheme [5] using the Williams-Soler [6] algorithm for the update of the wavefunctions. Our calculations used fully separable, norm-conserving pseudopotentials to describe the electron-ion interaction, constructed from an all-electron atomic calculation with the LDA functional. By applying Gonze's analysis [7] we confirmed that unphysical ghost states were not present in the separable representation. The wave functions were expanded in a plane wave basis with a cutoff energy of 40 Ry, and the **k**-space integration was performed with three special

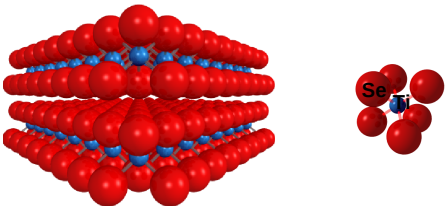

Figure 2. Schematic crystal structure of a transition metal dichalcogenide (TMDC) with a constituent section of octahedral symmetry at right.

k points in the surface Brillouin Zone. All calculations were done with slabs consisting of 3 or 4 atomic layers. The topmost two or three layers were free to relax in the structure optimization simulations, while the remaining bottom layers were fixed at their bulk positions. To model the surfaces a minimum of 28 atoms were used, which lead to 23042 plane waves and an overall memory requirement of 200 MB. This calculation takes about 3 hrs on 64 nodes of the T3E Cray at NIC. When steps are included in the simulations around 50 atoms with 70000 plane waves were required, taking about 8 hrs. on 128 nodes of the same computer. In a typical case, e.g. intercalation or diffusion, we used about 50 points to calculate the total path which multiplies the above given time by a factor of 50.

4 Properties of Substrate Material

The transition metal dichalcogenides appear in several closely related structural forms a single variant, namely 1T-$TiSe_2$, may suffice to explain their main features. The structure looks like the schematic drawing in Fig. 2 composed of Se-Ti-Se sandwiches assembled on top of each other along the [0001] direction, the sandwich normal direction. The separation of about 3 Å between the sandwiches is called the van der Waals gap denoting the very weak attractive forces of van der Waals type between them. In contrast, the intrasandwich separation between the single atomic layers belonging to the Se and Ti constituents is about half of that distance and is accompanied by a strong covalent attraction.

The lattice structure can be viewed as a hexagonal arrangement of the $TiSe_2$ units to form such a sandwich which constitutes then the solid by stacking. The top view of the surface shows a hexagonal mesh of Se atoms with the Ti atoms of the subsurface layer lying below the center of every second triangle. The atoms of the Se lower plane of the surface sandwich are situated below the remaining centers with the vertical distance being about 1.5 Å between two adjacent planes.

The intrasandwich binding consists of Ti spending 4 electrons from the partially filled atomic 3d shell and doubly occupied outer 4s shell (atomic configuration $3d^2 4s^2$) to the two Se atoms constituting the molecular unit $TiSe_2$ each of them completing its outer shell (atomic configuration $4s^2 p^4$) to Se^{-2}. This rough molecular picture is refined by band theory yielding all Se valence bands being almost filled (twice with respect to one Se-s and three Se-p bands, corresponding to eight electrons, of each of both Se constituents) leaving the Ti valence bands nearly empty. The importance of missing a full depletion of the Ti 3d shells and completion of the Se 4p shells lies in the instability of these compounds towards formation of charge density waves with subsequent phase transition. It is

described by so-called holes in the energetically uppermost valence bands and pockets in the lowermost conduction bands with momenta around specific points near the Fermi energy of the Brillouin zone. Especially, these momenta characterize the wave vector of the associated charge density wave excited by electronic transitions betwen pocket and hole. This instability is the stronger the closer the electronic structure is to pure two-dimensional behavior.

Thus, also for the phase transitions, the material's two-dimensionality is the driving force as it obviously is for a variety of other attractive features. For example, the easy cleavage along an intersandwich plane (along the van der Waals gap) results from the nearly saturated binding within a sandwich and yields the material's suitabilty as lubricant.

The most prominant feature we are interested in is represented by the perfectness of the (0001) surfaces of the TMDCs. Nowadays scanning tunneling microscopy reveals their faultless surface on atomic scale. Surface reconstructions as widely known from metals and semiconductors are absent in these materials, only slight relaxations of the layer distances at the surface occur. As a consequence, they offer for controlled surface physics and chemistry on nanoscale provided the combination with the desired species as adsorbate can be realized. Alkali atom adsoption has been well investigated in the past and to some extent also noble metal atom adsorption. Almost nothing is known about molecular adsorption on these substrates.

The first aim of our DFT calculations was to verify the bulk structure and to compare the crystal parameters with data known from experiment. As no precursor total energy studies were available we had to construct suitable pseudopotentials for reasonably fast convergence at tolerable accuracy. The transferability of the potentials had to be proved as well. We encountered difficulties which delayed progress in the very first stage eventually finding well working pseudopotentials for Ti and Se where the precision in the total energy could be held around 30 meV per atom. After these developments we found agreement with the experimental lattice parameters at theoretical values slightly lower (2-4%) and typical for DFT calculations. Lithium was considered as the first candidate to be investigated on adsorption. A lot of experimental information was available with respect to adsorption and intercalation. Furthermore, the compound Li_xTiSe_2 also had been experimentally investigated which we utilized to compare with our calculated $LiTiSe_2$ data verifying the procedure at a similar accuracy as in the case of $TiSe_2$.

5 Atom Adsorption and Diffusion on Plain Surfaces and in Intersandwich Gaps

Sites and energies of adsorption and diffusion were determined for the whole series of alkali atoms, Cu, and Au on $TiSe_2$[8]. A binding takes place and the adsorption sites are found at the hcp and fcc positions both with similar adsorption energy, hcp being slightly preferred. These sites refer to positions vertically above a Ti atom and a hole, resp., in the Ti layer, i.e. in the second atomic layer from the surface. Comparing the electron charge distribution of the relaxed system, substrate and adsorbate, with that of the individual constituents' electonic configuration at the final positions a shift of charge from the adsorbate atom onto the bonding region reaching into the interior of the solid is observed. This hints at a covalent bonding, not to be expected for TMDC surfaces where a physisorption concomitant with some polarization rather than a chemisorption should bind the adsorbate.

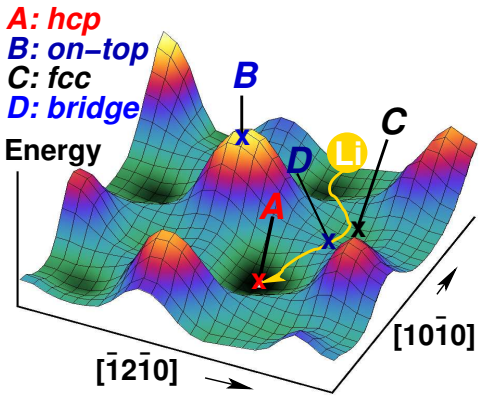

Figure 3. Energy landscape and minimum path of diffusion for Li on $TiSe_2(0001)$, color denotes energy heights; path leads from absolute minimum at hcp position (above Ti) at -3.03 eV across barrier with bridge position at -2.77 eV to fcc position (above hole of Ti layer) at -2.99 eV adsorption energy.

The diffusion path of such an adsorbed atom is illustrated in Fig. 3 demonstrating the low energy barrier of about 250 meV in the case of Li for surmounting the bridge position in diffusion.

This is sufficient for appreciable surface diffusion at room temperature which is important with respect to the type of growth of adsorbate layers on TMDCs. According to their increasing atomic size going from Li to Cs the vertical distance of the adsorbate from the surface plane increases also, thereby decreasing the activation energy of diffusion to almost zero (10 meV) in the case of Cs.

The situation for diffusion in the gap is quite similar to that on the surface regarding the shape of the energy surface which we calulated for Li in $TiSe_2$ as shown in Fig. 4. There are two equilibrium sites, the octahedral and tetrahedral position (see section 6) in the intersandwich gap, whose adsorption energies, 3.58 eV and 3.22 eV, differ more than those at the surface and are by about 0.5 eV higher than there. The barrier between both equilibrium positions of about 0.4 eV is appreciably higher than for Li at the surface. Thus, diffusion is delayed in the gap which may be expected because a plane of Se atoms limits the diffusion path on both sides, above and below.

We calculated the structural changes for varying content of Li in the gap, i.e. Li_xTiSe_2 concerning the uppermost sandwich including the gap below. As a result, the intersandwich gap increases by more than 10% with increasing content (x=0.06, 0.11, 0.25, 0.33, 0.50, 1.00) and the sandwich width of the adjacent sandwiches decreases by a little less than 5%. A widening of the gap could be expected, of course and that it occurs with a shrinking of the neighborhood, could foreseen too. The quantitative values and the confinement of the relaxation to the neighboring sandwiches had to be calculated.

The distinctly lower energy at the stable equilibrium position in the gap compared with the adsorption energy at the surface favors an intercalation, however, as shown in section 6 the direct intercalation path from the surface is hindered by a high energy barrier.

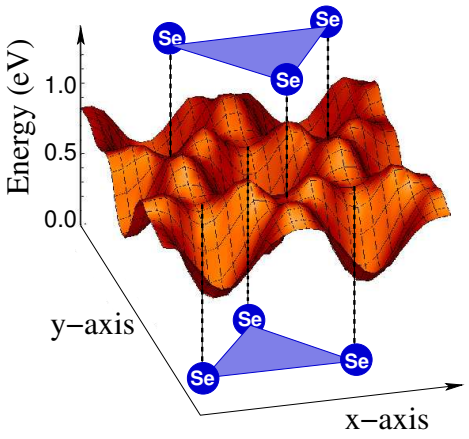

Figure 4. Energy landscape for diffusion of Li within intersandwich gap of $TiSe_2$, lower layer Se atoms of upper sandwich and upper layer Se atoms of lower sandwich frame intersandwich gap.

6 Intercalation from Plain Surface into Intersandwich Gap

From experiment, intercalation of Li into TMDC crystals was well established. However, the detailed circumstances under which such an intercalation takes place were not known. The primary problem was to investigate whether intercalation could proceed from an ideal unperturbed surface. Such intercalation should start at one of both equilibrium surface adsorption sites, hcp or fcc, the successive propagation being deduced from the evaluated minimum total energy for a sequence of values of depth z below the surface. The x, y directions of the propagating atom as well as the positions of the host atoms thereby are let free to relax. Fig. 5 shows this minimum path which first vertically runs against an energy barrier and then energetically glides downhill towards the center of the intersandwich gap. There are two minima within the gap, the octrahedral site given by the center between the framing Se atoms in Fig. 4 and the tetrahedral site perpendicularly in line with one of the Se atoms (above or below) in the intersandwich gap. The intermediate state after intercalation in Fig. 5 ends in a tetrahedral position whereas the terminal state of lowest energy is reached after further diffusion crossing a slight barrier of 0.06 eV to the octahedral site at an energy of -0.55 eV relative to energy zero at the hcp surface position.

This picture of an intercalation process from an ideal surface that results in an energy barrier of 3.81 eV to be surmounted does not admit any physical intercalation at moderate temperatures. Thus, the experimentally found intercalation processes must be associated with defects, such as steps or dislocations at the surface, if not entirely occurring via a penetration from the sides into the intersandwich gap, i.e. perpendicularly to (0001). Some results along these ideas are described in the next section.

7 Role of Surface Step Edges for Intercalation

There is experimentally strong evidence of intercalation so other mechanisms must be found. It is suggestive to look for surface defects, and we studied the role of step edges.

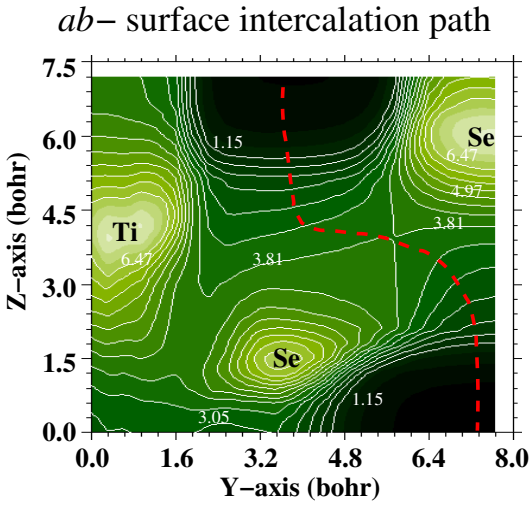

Figure 5. Intercalation path (dashed red line) in plane parallel to (0001) containing upper Se, Ti , and lower Se, starting at surface hcp adatom site with $z = 9.15$ a$_B$ and zero relative energy, crossing a high barrier of 3.81 eV at the saddle point, and terminating at the tetrahedral site with $z = -1.7$ a$_B$ in center of sandwich gap with relative energy -0.19 eV; contour plot with level spacing of 0.38 eV.

From STM experiment, steps are found along the high symmetry directions which can be reduced to two specific types of edges. One of these is displayed in Fig. 6 together with some special positions of a Li adatom diffusing across the step and with positions during entering the intersandwich gap. The Li diffusion proceeds as stated in section 5 through the hcp, bridge, fcc, bridge sites sequentially repeated up to the step edge. The Li atom then keeps bounds to both last upper Se atoms at equal distance, and dropping down, it turns for binding towards the two Se atoms which lie tilted by 60° in the lower plane. From there it may diffuse on the lower sandwich terrace or enter the intersandwich gap as shown in Fig. 6. The energies for these steps and their corresponding heights are shown in Fig. 7. The astonishing fact in this plot is the complete absence of a so-called Schwoebel barrier. It is usually encountered by an atom diffusing towards an edge because beyond the edge atoms are missing which would attract and bind. In other words, a missing attraction from beyond the step means a repulsion by the step edge for the approaching atom. This would show in an extra energy barrier higher than the maximum diffusion barrier, which is not observed in this case.

8 Molecular Chemisorption contra Picture of Inert Surface Material

In the common view the TMDC surfaces are chemically inert. Doubts have been already raised in the context of section 5. We investigated a class of chemical compounds containing AuCl which is able to bind to various molecular groups. The simplest compound AuCl proved suitable to be bound by a $TiSe_2$ surface as was also the case for the more complicated PH_3AuCl of which we show a selection of configurations in Fig. 8 together

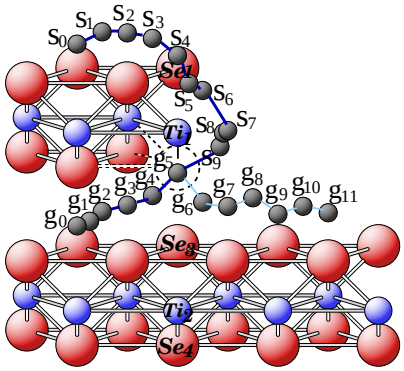

Figure 6. Diffusion of Li across a $TiSe_2$ surface step, on upper terrace (S_0–S_9) and lower terrace (g_5–g_{11}), and path for entering intersandwich gap (g_5–g_0); imagine uppermost sandwich as halfway laterally truncated, the lower fully extended; note that lower Se would cover view of Li g_5 position, atom and its binding bars are therefore sketched only by broken lines. The cut through the crystal to generate this edge can be viewed by fixing an surface plane Se triangle which contains a Ti below its center as seen from above the surface. The perpendicular from one of the three corner Se atoms onto the opposite triangle side aligns with this cut which extends vertically through the first sandwich and meets one of the lower Se atoms belonging to the same octahedron around the Ti atom.

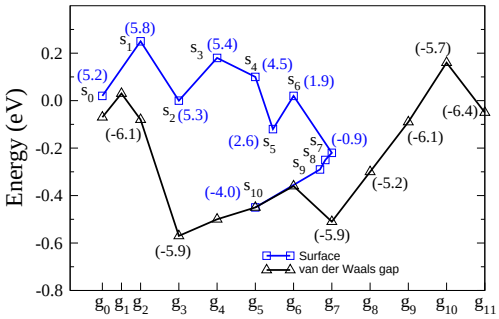

Figure 7. Energy for diffusion of Li across a $TiSe_2$ surface step, see Fig. 6, numbers in parentheses denote height in a_B with respect to Ti plane.

with their energy. From the 6 configurations 5 are seen to be bound by the surface.

From the findings of our calculations we suggest that indeed chemisorption takes place for this type of molecules opening a new path for surface chemistry because the variability of molecular groups which can be appended at AuCl is vast.

9 Conclusions

The study of adsorption on layered transition metal dichalcogenides by ab initio density functional theory has answered various questions as to how the diffusion and intercalation can proceed and which the activation energies for the single processes are. Further results, e.g with respect to growth of total layers, are not presented here because of lacking space.

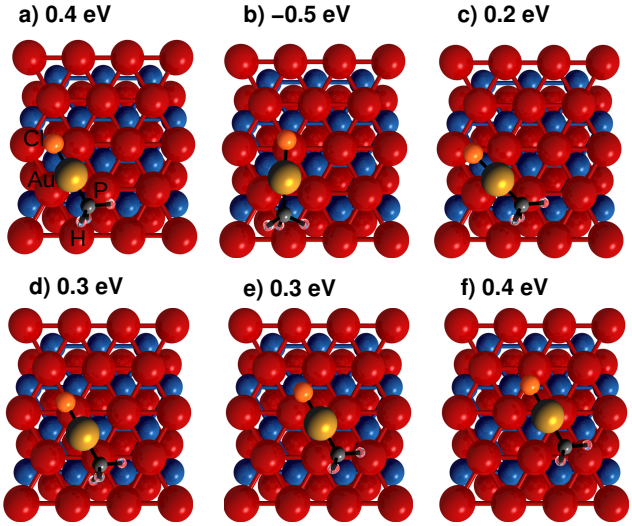

Figure 8. Various positions for PH_3AuCl molecule and binding energy, molecule colored as Au (yellow), Cl (orange), P (grey), H (light) and substrate Ti (blue), Se (red).

The calculations delivered quantitative results, partly to be expected partly astonishing, which to our opinion are decisive for the interpretation of actual experiments in this field. In addition, a perspective for physical and chemical reaction mechanisms to be suggested for future processing has emerged.

Acknowledgments

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References

1. R. Adelung, J. Brandt, K. Roßnagel, O. Seifarth, L. Kipp, M. Skibowski, C. Ramírez, T. Strasser, and W. Schattke, Phys. Rev. Lett. **86**, 1303 (2001).
2. E.E. Krasovskii, in *Solid-State Photoemission and Related Methods* ed. by W. Schattke and M.A. Van Hove (Wiley-VCH, 2003).
3. M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comp. Phys. Comm. **107**, 187 (1997).
4. N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
5. R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
6. A. Williams and J. Soler, Bull. Am. Phys. Soc. **32**, 562 (1987).
7. X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).
8. C. Ramírez and W. Schattke, Surf. Sci. **482-485**, 424 (2001).